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The Viscosities of Melts in the $PbCl_2$ - KCl - NaCl and $PbCl_2$ - KCl - LiCl System

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Abstract

The viscosity of $PbCl_2$ - KCl - LiCl were determined by a Brookfield Digital Viscometer, over a temperature range of 730-1140 K.

The viscosity data obtained above 1000 K may not be reliable due to the high vapourization of $PbCl_2$ in the mixture.

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INTRODUCTION

Currently, lead is extracted from lead sulphide concentrates by a process that involves sintering, followed by high temperature carbon reduction in a blast furnace. This method provides an energy-efficient, low-cost method for producing lead metal. Unfortunately, it also leads to several environmental concerns such as sulphur dioxide production and the emissions of heavy metals. Many new processes have appeared in the literature which try to ameliorate these environmental problems. One such process is the conversion of galena (PbS) to lead chloride ($PbCl_2$), followed by fused-salt electrolysis to produce lead metal [1].

Lead chloride itself is not an adequate electrolyte for this new process since it has a high vapour pressure, a high melting point, and it exhibits poor current efficiency with respect to lead production. The ternary systems $PbCl_2$-KCl-NaCl and $PbCl_2$-KCl-LiCl have been suggested as possible electrolytes. The $PbCl_2$-KCl-LiCl system has a higher molar conductivity, but due to the hygroscopic nature of LiCl, the $PbCl_2$-KCl-NaCl system may be a more desirable alternative.

Recently, the surface tensions and densities for both of these ternary systems have been reported in the literature [2,3]. As an extension of this work, the viscosities of the $PbCl_2$-KCl-NaCl and the $PbCl_2$-KCl-LiCl

systems were investigated.

EXPERIMENTAL

Apparatus

A schematic diagram of the apparatus used in this study is shown in Figure 1. The main features include a Brookfield Digital Viscometer (model LVTD), a suspension system for an outer crucible, a molybdenum wire which transmits the torque from the viscometer to the platinum spindle, a molybdenum wound furnace, and a lifting system. A large neoprene bellow was added in order to isolate the system from the outside atmosphere. The temperature of the furnace was controlled by a 'West SCR Controller' to within $\pm 0.5^{o}K$. The maximum temperature variation in the furnace's hot-zone was $\pm 2^{o}K$ at all temperatures investigated. The spindles were calibrated against liquid $PbCl_2$, $PbCl_2$-KCl mixtures, and KCl-NaCl. The rotational speed was 60 rpm.

Melt Preparation

Reagent grade NaCl, $PbCl_2$, KCl, and LiCl salts were used throughout this study. Owing to the hygroscopic nature of LiCl, this salt was stored in an oven at 425 K.

The desired melts were prepared by mixing preweighed pure salts which were dried in a current of dry HCl at 600-700 K. After approximately 2-3 hours, the temperature was increased in order to melt the salts. Dried HCl was passed through the melts for another 3 hours. Melts were

then cast into pellets for use in the viscosity experiments.

Calibration

The calibration of the viscometer was performed using the following liquids: $PbCl_2$, $PbCl_2$-KCl (66.4 mol % $PbCl_2$), $PbCl_2$-KCl (48.9 mol % $PbCl_2$), $PbCl_2$-KCl (33.4 mol % $PbCl_2$), $PbCl_2$-KCl (25.9 mol % $PbCl_2$), and NaCl-KCl (72.9 mol % NaCl). Viscosity data for these particular liquids are well established [4]. The chosen standard liquids were purified according to the aforementioned procedure, and then placed in a platinum crucible, which in turn was placed into a molybdenum outer crucible. The outer crucible was fastened onto an alumina holder with molybdenum pins and the furnace was slightly raised in order to allow the clamping of the neoprene bellow to the top cap of the furnace. Purified Ar gas was admitted into the furnace and then the furnace itself was raised to its final position. The system was flushed with purified Ar for 10-12 hours while the furnace temperature was approximately 600 K. Afterwards, the furnace temperature was raised to the highest temperature for which viscosity data are available [4]. At this point, the spindle was lowered into the melt and maintained at a fixed position. After the data were recorded, the temperature of the furnace was lowered in 10-20^{o}K increments and further viscosity data were recorded.

The volume of each sample was approximately 50 ml. The

volume was estimated using density data for the system.

RESULTS

The results from the calibration procedure are presented in Table 1. This data cannot be treated by conventional techniques to produce an equation which relates viscosity to the torque reading. It can easily be seen that for a constant viscosity, the torque readings are different, and depend on the composition of the salt. In order to produce a calibration curve, the following technique was employed.

It was assumed that the viscosity of the melt (η) is related to the torque reading by:

$$\eta = ((\text{Reading}/f(\text{Density}))^K$$

Using a regression analysis [5] it was determined that:

$$f(\text{Density}) = -0.482 + 3.329\ \rho - 0.240\ \rho^2$$

and that 'K' is approximately 2.36. The calibration curve obtained is shown in Figure 2. Based on the 96 data points for 6 different systems (see Table 1), a correlation coefficient (r) of 0.995 was obtained for the line shown in Figure 2. The density data used in this analysis are shown in Table 2.

The $PbCl_2$-KCl-NaCl System

The experimental data for the $PbCl_2$-KCl-NaCl system are

shown in Tables 3-6. The 't' parameter is defined as:

$$t = \frac{X_{NaCl}}{X_{NaCl} + X_{KCl}}$$

where 'X' represents mole fraction. The viscosity values were determined using the calibration curve shown in Figure 2. These results are presented graphically in Figures 3-6 for various y-values ($y=1-X_{PbCl_2}$). The density data for these systems are also summarized in Table 2. For each curve, the viscosity decreased with increasing temperature.

The $PbCl_2$-KCl-LiCl System

The experimental data for the $PbCl_2$-KCl-LiCl system are presented in Tables 7-10. For this system, the 't' parameter is defined as:

$$t = \frac{X_{LiCl}}{X_{LiCl} + X_{KCl}}$$

and 'y' is still defined as:

$$y = 1 - X_{PbCl_2}.$$

The corresponding viscosity curves are presented graphically in Figures 7-10.

In order to generate the viscosity curves, reliable density data for the various systems must be available. In

order to obtain the density of the melt at the desired composition, some extrapolation of the density values found in the literature was necessary.

Owing to the high vapour pressure of $PbCl_2$, some of the viscosity measurements may not be reliable above 1000 K.

REFERENCES

[1] M.M. Wong, F.P. Haver, and R.G. Sandberg: "Ferric Chloride Leach-Electrolysis" in Lead-Zinc-Tin '80, TMS-AIME, pp. 445-454.

[2] G. Liu, T. Utigard, and J.M. Toguri: J. Chem. Eng. Data, Volume 31, pp. 342-346 (1986).

[3] T. Fujisawa, T. Utigard, and J.M. Toguri: Can. J. Chem., Volume 63(5), pp. 1132-1138 (1985).

[4] G.S. Janz, R.P.T. Tomkins, C.B. Allen, J.R. Downey Jr., G.L. Gardner, U. Krebs, and S.K. Singer: J. Phys. Chem. Ref. Data, Volume 4(4), pp. 871-1178 (1975).

[5] M. Ezekiel and K.A. Fox: "Methods of Correlation Analysis (3^{rd} edition)", John Wiley & Sons, Inc., New York (1970).

[6] N.K. Boardman, F.H. Dorman, and E. Heymann: J. Phys. & Colloid Chem., Volume 53, pp. 375-382 (1949).

[7] A. Gutierrez and J.A. Toguri: J. Chem. Eng. Data, Volume 27(2), pp. 109-113 (1982).

[8] A. Gutierrez Palacios: "Densities and Molar Volumes in the $PbCl_2$-KCl-NaCl and $PbCl_2$-KCl-LiCl Ternary Systems", M.A.Sc. Thesis, Department of Metallurgy and Materials Science, University of Toronto (1980).

TABLE 1

Calibration Results for $PbCl_2$

Temperature (K)	Reading (mV x 10)	Viscosity (mPa s)
780	19.30, 19.20	4.44
800	18.05, 18.01	3.98
820	17.32, 17.09	3.58
840	16.49, 16.32	3.24
860	15.77, 15.71	2.95
880	14.98, 15.10	2.69
900	14.47, 14.46	2.47
920	14.00, 13.99	2.27
940	13.45, 13.50	2.10
960	13.06, 13.09	1.95

Calibration Results for $PbCl_2$-KCl (66.4 mol % $PbCl_2$)

Temperature	Reading (mV x 10)	Viscosity (mPa s)
730	17.04	4.42
750	16.16	3.94
770	15.40	3.53
790	14.62	3.18
810	13.83	2.89
830	13.17	2.63
850	12.57	2.40
870	12.29	2.20
890	11.71	2.03
910	11.37	1.88
930	11.00	1.74
950	10.67	1.62
970	10.58	1.52

TABLE 1 (CONTINUED)

Calibration Curve for $PbCl_2$-KCl (25.9 mol % $PbCl_2$)

Temperature	Reading (mV x 10)	Viscosity (mPa s)
930	7.98, 7.87, 8.00	1.76
940	7.72, 7.75, 7.77	1.70
950	7.66, 7.65, 7.68	1.63
960	7.46, 7.52, 7.55	1.57
970	7.38, 7.35, 7.35	1.51
980	7.25, 7.21	1.46 (*)
990	7.10, 7.15	1.41 (*)
1000	7.03	1.36 (*)
1010	6.86, 6.85	1.31 (*)
1020	6.85, 6.81	1.27 (*)
1030	6.65, 6.65	1.23 (*)

(*) - calculated from the equation given in[4]

Calibration Curve for NaCl-KCl (72.9 mol % NaCl)

Temperature	Reading (mV x 10)	Viscosity (mPa s)
1000	5.25, 5.19	1.78
1020	4.97, 5.05	1.63
1040	4.86, 4.84	1.50
1060	4.74, 4.76	1.39
1080	4.66, 4.65	1.29
1100	4.45, 4.48	1.19
1120	4.33, 4.36	1.11
1140	4.36, 4.23	1.04

TABLE 1 (CONTINUED)

Calibration Results for $PbCl_2$-KCl (48.9 mol % $PbCl_2$)

Temperature	Reading (mV x 10)	Viscosity (mPa s)
730	15.14	4.36
750	14.41	3.89
770	13.65	3.47
790	13.07	3.11
810	12.50	2.80
830	12.04	2.53
850	11.50	2.29
870	11.15	2.10
890	10.58	1.93
910	10.29	1.80
930	10.03	1.68
950	9.76	1.58
970	9.67	1.50

Calibration Results for $PbCl_2$-KCl (33.4 mol % $PbCl_2$)

Temperature	Reading (mV x 10)	Viscosity (mPa s)
830	10.93	2.56
850	10.46	2.36
870	10.10	2.17
890	9.72	2.01
910	9.27	1.85
930	9.00	1.72
950	8.72	1.60
970	8.50	1.49

TABLE 2 - DENSITY DATA USED

CALIBRATION

A	B		SYSTEM	
6.112	-15.0	[4]	$PbCl_2$	
2.137	-5.59	[4]	NaCl-KCl	(72.9 mol % NaCl)
3.37	-8.9	[6]*	$PbCl_2$-KCl	(25.9% $PbCl_2$)
3.69	-9.76	[6]*	"	(33.4% $PbCl_2$)
4.32	-11.40	[6]*	"	(48.9% $PbCl_2$)
4.97	-13.0	[6]*	"	(66.4% $PbCl_2$)

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3.219	-10.1	[7]	$PbCl_2$-KCl-NaCl	(t=0.25, y=0.8)
3.105	-7.4	[7]	"	(t=0.50, y=0.8)
3.219	-8.2	[7]	"	(t=0.75, y=0.8)
4.098	-10.5	[7]*	"	(t=0.25, y=0.6)
3.969	-9.4	[7]	"	(t=0.50, y=0.6)
4.235	-10.4	[7]*	"	(t=0.75, y=0.6)
4.28	-7.0	[3]	"	(t=0.25, y=0.4)
4.920	-13.7	[7]	"	(t=0.50, y=0.4)
4.86	-12.0	[3]	"	(t=0.75, y=0.4)
5.44	-13.7	[8]*	"	(t=0.25, y=0.2)
5.86	-14.0	[3]	"	(t=0.50, y=0.2)
5.56	-14.0	[8]*	"	(t=0.75, y=0.2)
3.03	-7.0	[8]*	$PbCl_2$-KCl-LiCl	(t=0.25, y=0.8)
2.932	-7.5	[7]	"	(t=0.50, y=0.8)
3.471	-10.9	[7]	"	(t=0.75, y=0.8)
4.060	-10.6	[7]	"	(t=0.25, y=0.6)
4.066	-9.8	[7]	"	(t=0.50, y=0.6)
4.195	-10.4	[7]	"	(t=0.75, y=0.6)
4.814	-12.5	[7]	"	(t=0.25, y=0.4)
5.015	-14.0	[7]	"	(t=0.50, y=0.4)
4.957	-12.0	[7]	"	(t=0.75, y=0.4)
5.574	-15.0	[7]	"	(t=0.25, y=0.2)
5.296	-11.0	[7]	"	(t=0.50, y=0.2)
5.578	-14.0	[7]	"	(t=0.75, y=0.2)

$$\rho = A + B \times 10^{-4} T \quad \text{(density in g/ml; T in } ^{o}K)$$

* designates density data that has been extrapolated or deduced from the reference given

TABLE 3

$PbCl_2$-KCl-NaCl System (y=0.2)

	t=0.25		t=0.50		t=0.75	
T (K)	Reading mV x 10	Viscosity mPa s	Reading mV x 10	Viscosity mPa s	Reading mV x 10	Viscosity mPa s
760	16.93	3.89	16.88	3.47	16.56	3.59
780	16.00	3.44	16.04	3.10	15.86	3.27
800	15.19	3.07	15.00	2.66	15.22	2.99
820	14.65	2.84	14.42	2.44	14.28	2.60
840	13.56	2.39	13.70	2.18	13.31	2.22
860	13.00	2.18	12.75	1.85	12.56	1.95
880	12.32	1.94	12.19	1.68	12.02	1.77
900	11.97	1.83	11.75	1.55	11.49	1.61
920	11.51	1.68	11.40	1.46	11.03	1.47
940	11.09	1.55	11.10	1.38	10.64	1.37
960	10.86	1.49	10.70	1.27	10.36	1.29
980	10.65	1.44	10.27	1.17	10.08	1.22

TABLE 4

$PbCl_2$-KCl-NaCl System (y=0.4)

	t=0.25		t=0.50		t=0.75	
T (K)	Reading mV x 10	Viscosity mPa s	Reading mV x 10	Viscosity mPa s	Reading mV x 10	Viscosity mPa s
760	14.55	3.44	14.45	3.21	14.38	3.09
780	13.86	3.08	13.85	2.93	13.75	2.80
800	13.09	2.71	13.13	2.61	13.00	2.48
820	12.55	2.47	12.33	2.28	12.22	2.16
840	12.03	2.25	11.65	2.02	11.64	1.95
860	11.65	2.10	11.20	1.86	11.26	1.82
880	11.11	1.89	10.70	1.69	10.77	1.65
900	10.65	1.72	10.35	1.58	10.34	1.51
920	10.25	1.58	10.05	1.49	10.02	1.42
940	9.84	1.44	9.75	1.40	9.74	1.34
960	9.52	1.34	9.44	1.32	9.40	1.25
980	9.35	1.29	9.30	1.29	9.28	1.22

TABLE 5

$PbCl_2$-KCl-NaCl System (y=0.6)

	t=0.25		t=0.50		t=0.75	
T (K)	Reading mV x 10	Viscosity mPa s	Reading mV x 10	Viscosity mPa s	Reading mV x 10	Viscosity mPa s
860			9.71	1.76		
880			9.33	1.62		
890	9.25	1.57				
900			9.05	1.52		
910	8.84	1.42				
920			8.67	1.39	8.76	1.29
930	8.55	1.33				
940			8.28	1.26	8.49	1.22
950	8.14	1.20				
960			7.95	1.16	8.23	1.16
970	7.77	1.09				
980			7.65	1.07	8.05	1.10
990	7.54	1.03				
1000			7.38	0.99	7.81	1.03
1010	7.26	0.95				
1020			7.24	0.96	7.56	0.97

TABLE 6

$PbCl_2$-KCl-NaCl System (y=0.8)

	t=0.25		t=0.50		t=0.75	
T (K)	Reading mV x 10	Viscosity mPa s	Reading mV x 10	Viscosity mPa s	Reading mV x 10	Viscosity mPa s
980	6.84	1.51	6.90	1.35		
1000	6.61	1.42	6.66	1.26	6.93	1.34
1020	6.53	1.40	6.20	1.07	6.75	1.28
1040	6.43	1.38	5.83	0.94	6.59	1.22
1060	6.16	1.27			6.40	1.16
1080	6.04	1.24			6.16	1.07
1100	5.86	1.18			6.00	1.02
1120	5.71	1.13				

TABLE 7

$PbCl_2$-KCl-LiCl System (y=0.2)

T (K)	t=0.25 Reading mV x 10	t=0.25 Viscosity mPa s	t=0.50 Reading mV x 10	t=0.50 Viscosity mPa s	t=0.75 Reading mV x 10	t=0.75 Viscosity mPa s
740	17.56	4.16				
750			17.00	3.85		
760	16.47	3.61				
770			15.98	3.35		
780	15.64	3.23				
790			14.92	2.87		
800	14.76	2.84			14.36	2.59, 2.51
810			14.01	2.49		
820	14.00	2.53			13.65	2.32, 2.28
830			13.45	2.27		
840	13.24	2.24			12.80	2.01, 1.97
850			12.95	2.09		
860	12.67	2.04			12.25	1.83, 1.82
870			12.30	1.87		
880	12.14	1.86			11.75	1.67, 1.66
890			11.68	1.66		
900	11.76	1.74			11.32	1.54, 1.5
920					10.85	1.41, 1.4
940					10.57	1.34, 1.3
960					10.35	1.28, 1.27

TABLE 8

$PbCl_2$-KCl-LiCl System (y=0.4)

	t=0.25		t=0.50		t=0.75	
T (K)	Reading mV x 10	Viscosity mPa s	Reading mV x 10	Viscosity mPa s	Reading mV x 10	Viscosity mPa s
720			16.20	4.00		
740			15.10	3.42		
760	13.80	2.89	14.25	3.02		
780	13.06	2.57	13.43	2.65		
800	12.38	2.29	12.67	2.34	13.13	2.46
820	11.69	2.02	12.13	2.13	12.66	2.28
840	11.19	1.84	11.21	1.79	12.13	2.08
860			10.86	1.68	11.84	1.98
880	10.38	1.57	10.43	1.54	11.30	1.79
900	10.08	1.48	9.82	1.35	10.74	1.60
920	9.53	1.31	9.57	1.29	10.31	1.47
940	9.22	1.23	9.37	1.24	10.00	1.38
960	9.00	1.17	9.19	1.20	9.81	1.33
980			9.06	1.18		

TABLE 9

$PbCl_2$-KCl-LiCl System (y=0.6)

	t=0.25		t=0.50		t=0.75	
T (K)	Reading mV x 10	Viscosity mPa s	Reading mV x 10	Viscosity mPa s	Reading mV x 10	Viscosity mPa s
730	13.13	3.35				
750	12.43	2.98			13.97	3.63
770	11.66	2.59			13.24	3.23
790	11.00	2.28	11.73	2.56	12.66	2.94
810	10.44	2.04	11.03	2.24	12.00	2.62
830	9.90	1.82	10.55	2.04	11.40	2.35
850	9.35	1.61	10.00	1.81	10.90	2.13
870	8.95	1.47	9.50	1.62	10.40	1.93
890	8.59	1.35	8.75	1.35	10.10	1.82
910	8.28	1.25	8.35	1.22	9.80	1.71
930	7.97	1.16	8.00	1.12		
950	7.67	1.07	7.66	1.02	9.20	1.51
970	7.35	0.98	7.40	0.95		
990	7.18	0.94	7.16	0.89		

TABLE 10

$PbCl_2$-KCl-LiCl System (y=0.8)

	t=0.25		t=0.50		t=0.75	
T (K)	Reading mV x 10	Viscosity mPa s	Reading mV x 10	Viscosity mPa s	Reading mV x 10	Viscosity mPa s
780			9.50	2.95		
800			8.87	2.54		
820	8.55	2.10	8.40	2.26		
840	8.05	1.85	8.05	2.07		
860	7.55	1.61	7.80	1.95		
880	7.25	1.48	7.42	1.76	8.13	1.78
900	6.89	1.32	7.11	1.61	7.45	1.47
920	6.65	1.23	6.85	1.50	7.17	1.37
940	6.35	1.12	6.60	1.39	6.76	1.21
960	6.15	1.05	6.38	1.30	6.55	1.15
980	5.95	0.98	6.25	1.26	6.53	1.16
1000			6.00	1.16	6.40	1.13
1020					6.35	1.13

FIGURE CAPTIONS

1 Schematic diagram of the experimental apparatus.

2 Calibration curve obtained using various salts:

(1) $PbCl_2$ O ○

(2) $PbCl_2$-KCl (66.4 mol % $PbCl_2$) △

(3) $PbCl_2$-KCl (48.9 mol % $PbCl_2$) X

(4) $PbCl_2$-KCl (33.4 mol % $PbCl_2$) *

(5) $PbCl_2$-KCl (25.9 mol % $PbCl_2$) ◇

(6) NaCl-KCl (72.9 mol % NaCl) □

3 $PbCl_2$-KCl-NaCl System (y=0.2): t=0.25 (O); t=0.50 (X); t=0.75 (△).

4 $PbCl_2$-KCl-NaCl System (y=0.4): t=0.25 (O); t=0.50 (X); t=0.75 (△).

5 $PbCl_2$-KCl-NaCl System (y=0.6): t=0.25 (O); t=0.50 (X); t=0.75 (△).

6 $PbCl_2$-KCl-NaCl System (y=0.8): t=0.25 (O); t=0.50 (X); t=0.75 (△).

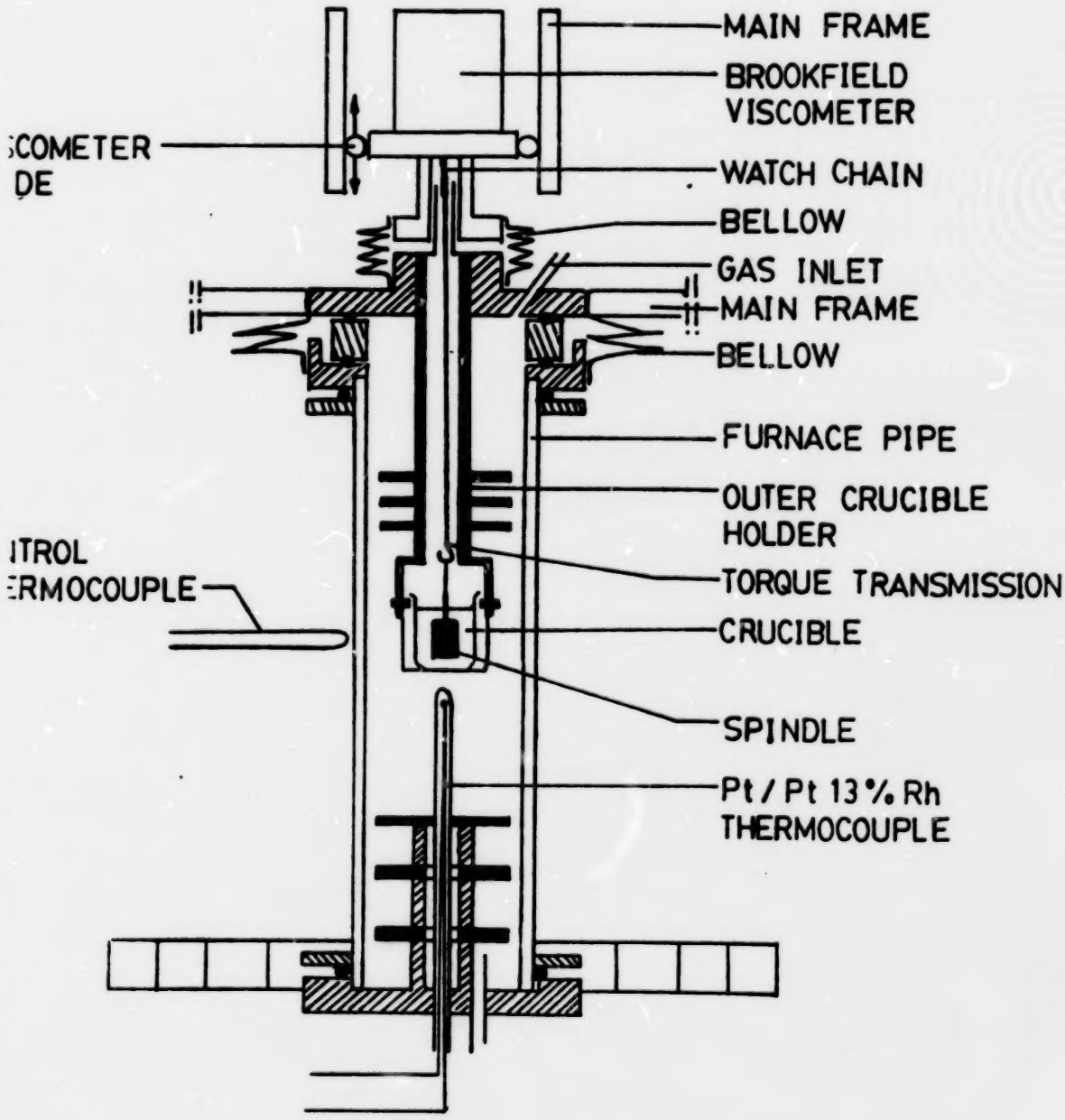
7 $PbCl_2$-KCl-LiCl System (y=0.2): t=0.25 (O); t=0.50 (X); t=0.75 (△).

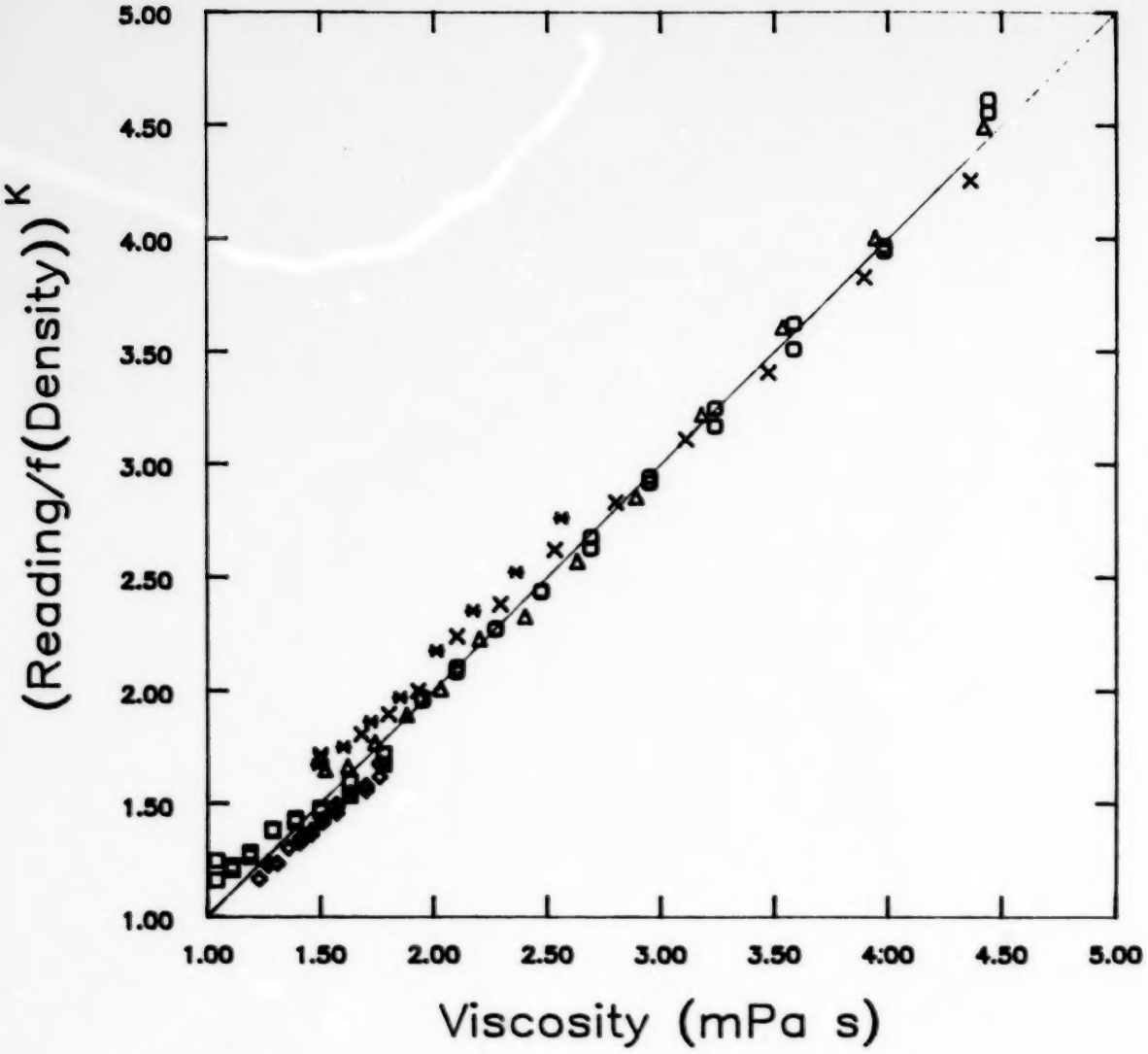
8 $PbCl_2$-KCl-LiCl System (y=0.4): t=0.25 (O); t=0.50 (X); t=0.75 (△).

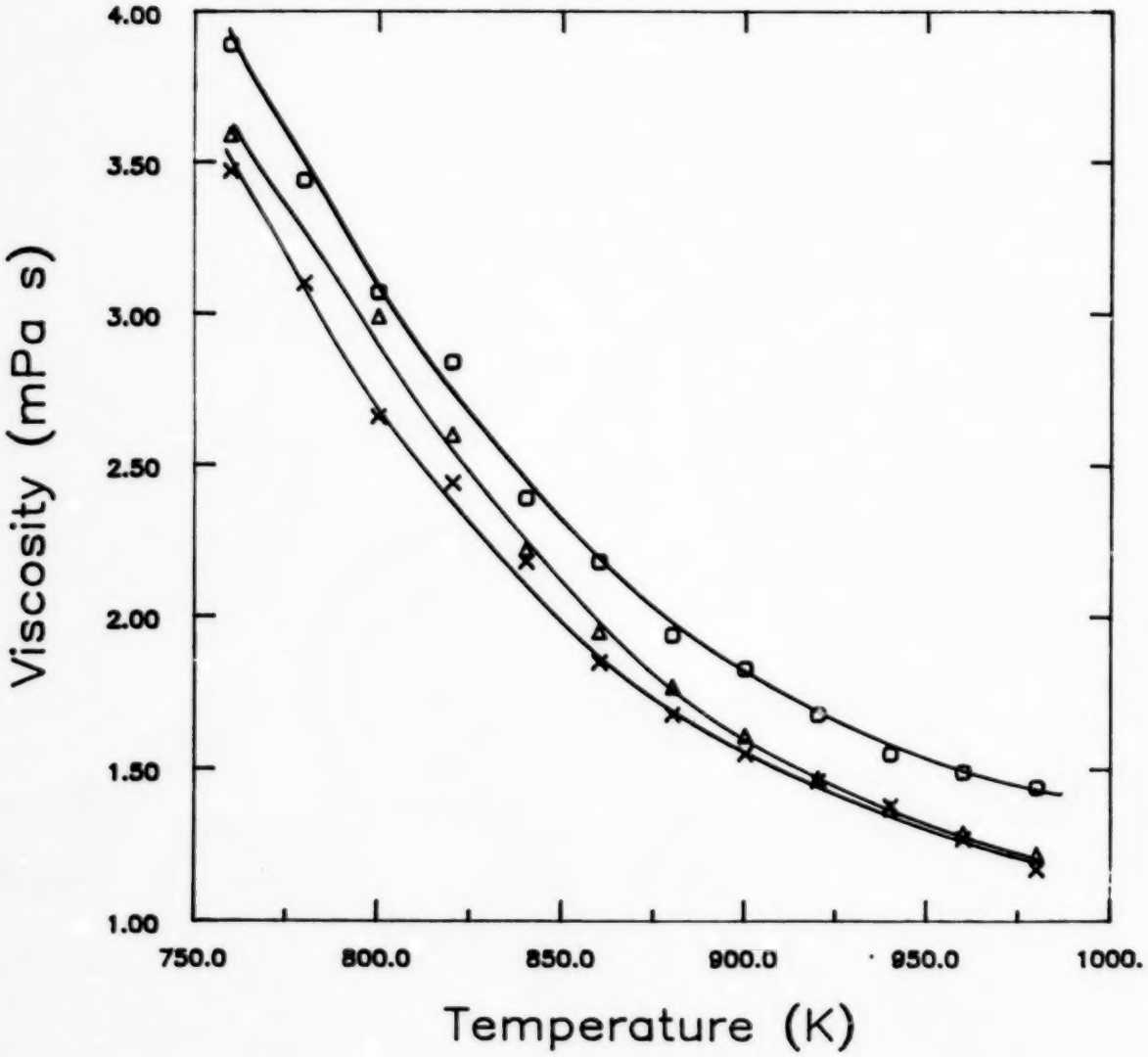
9 $PbCl_2$-KCl-LiCl System (y=0.6): t=0.25 (O); t=0.50 (X); t=0.75 (△).

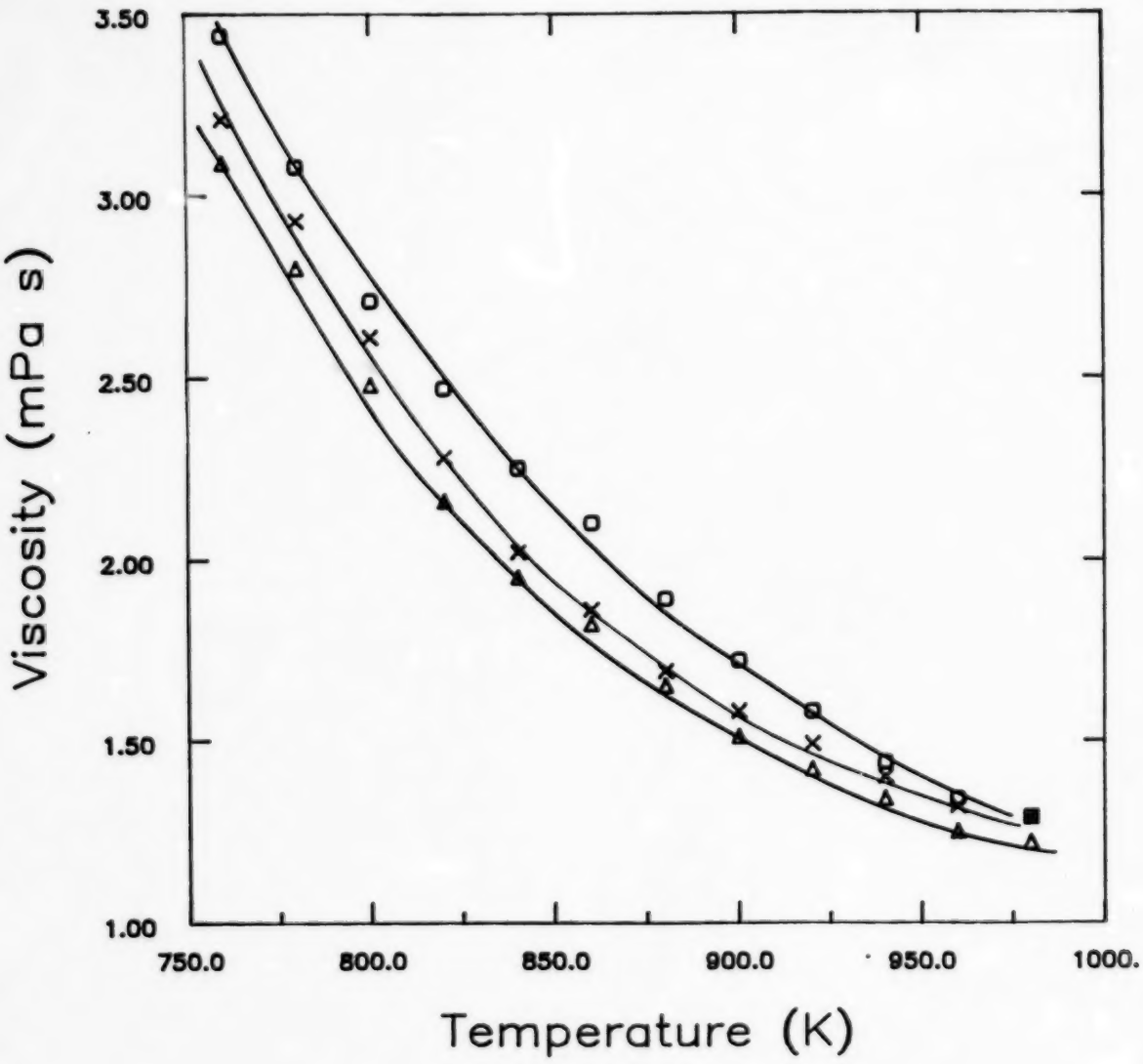
10 $PbCl_2$-KCl-LiCl System (y=0.8): t=0.25 (O); t=0.50 (X); t=0.75 (△).

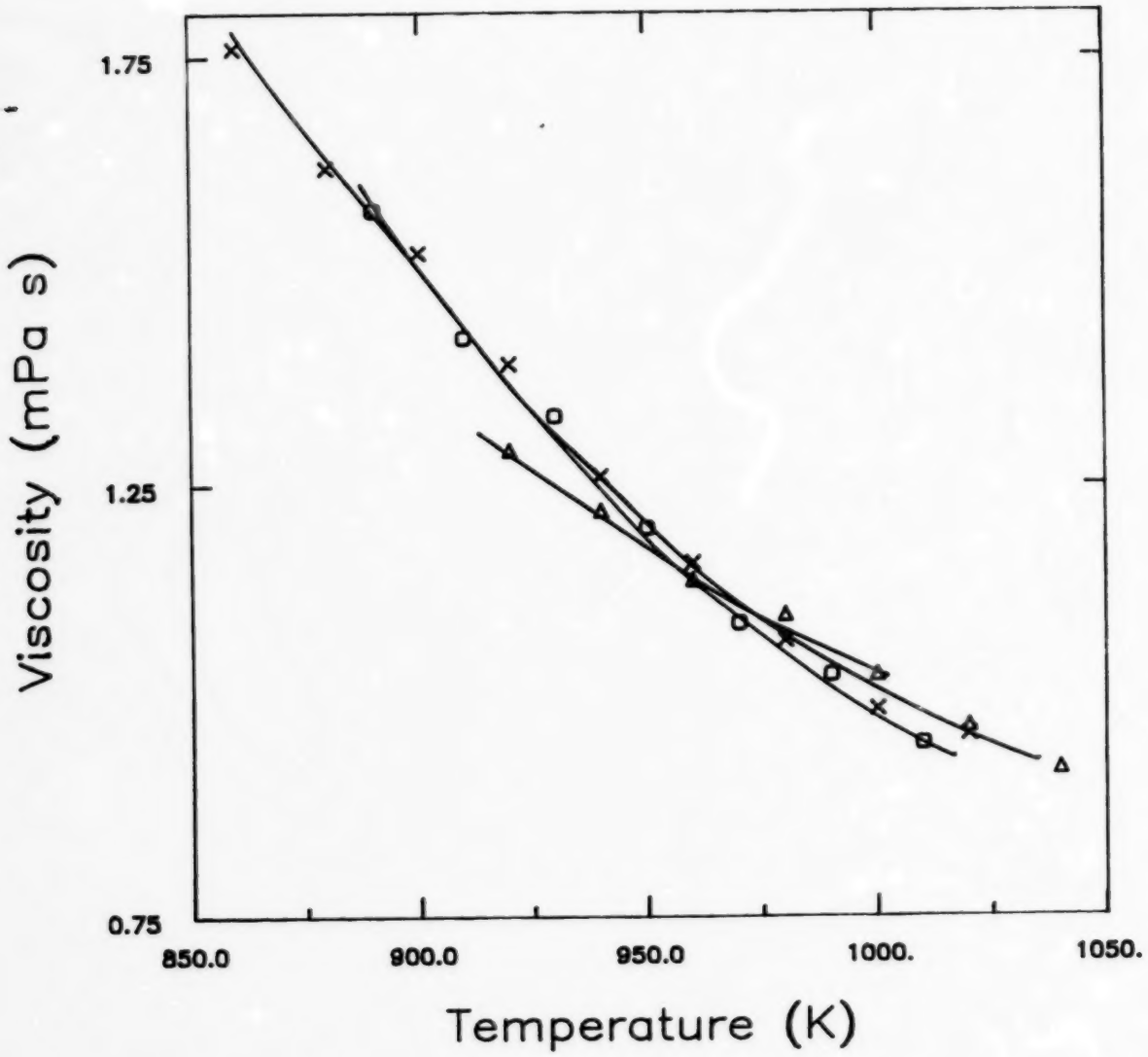
Fig 1

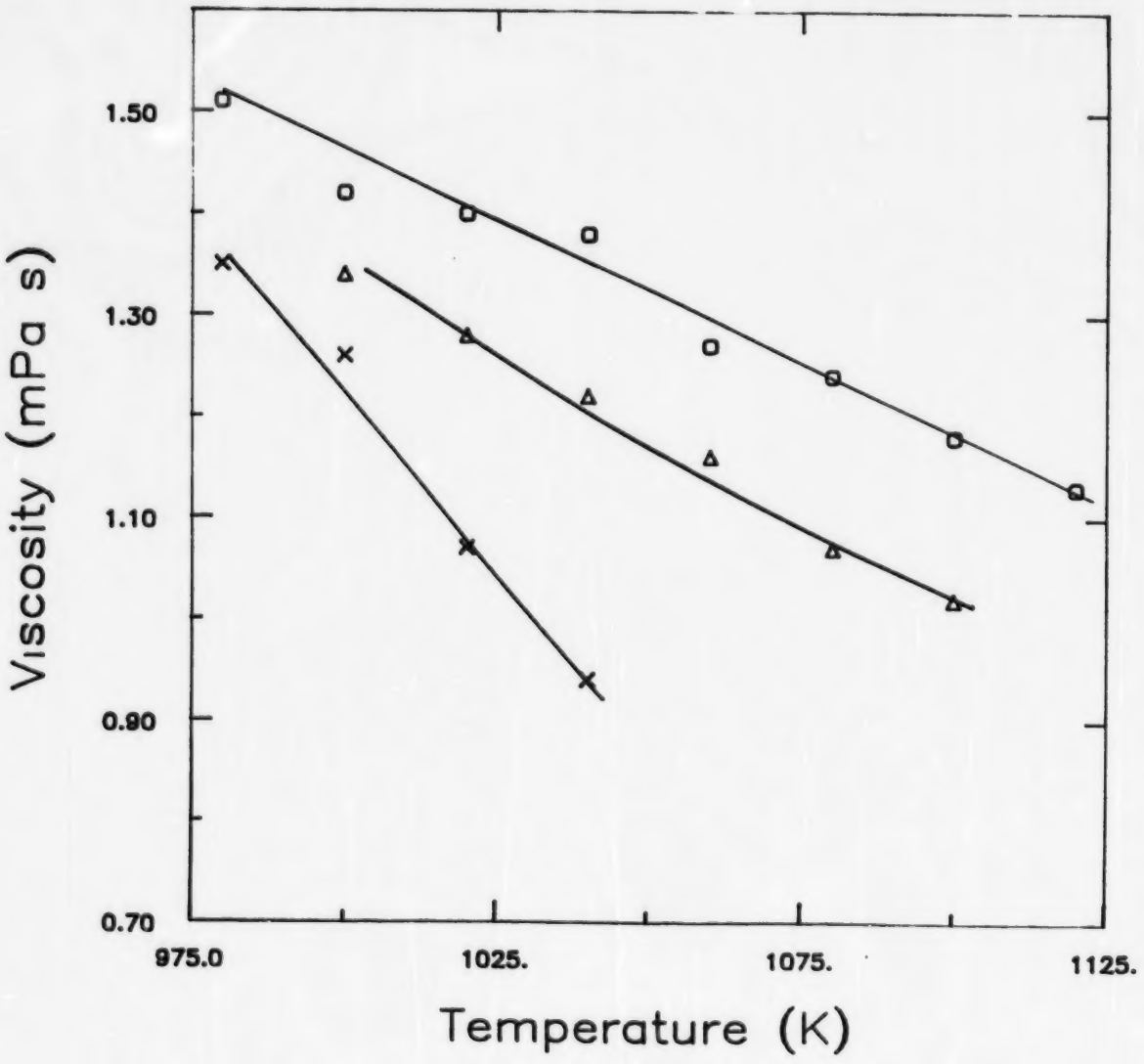

MAIN FRAME
BROOKFIELD VISCOMETER
WATCH CHAIN
BELLOW
GAS INLET
MAIN FRAME
BELLOW
FURNACE PIPE
OUTER CRUCIBLE HOLDER
TORQUE TRANSMISSION
CRUCIBLE
SPINDLE
Pt / Pt 13 % Rh THERMOCOUPLE
ITROL
ERMOCOUPLE

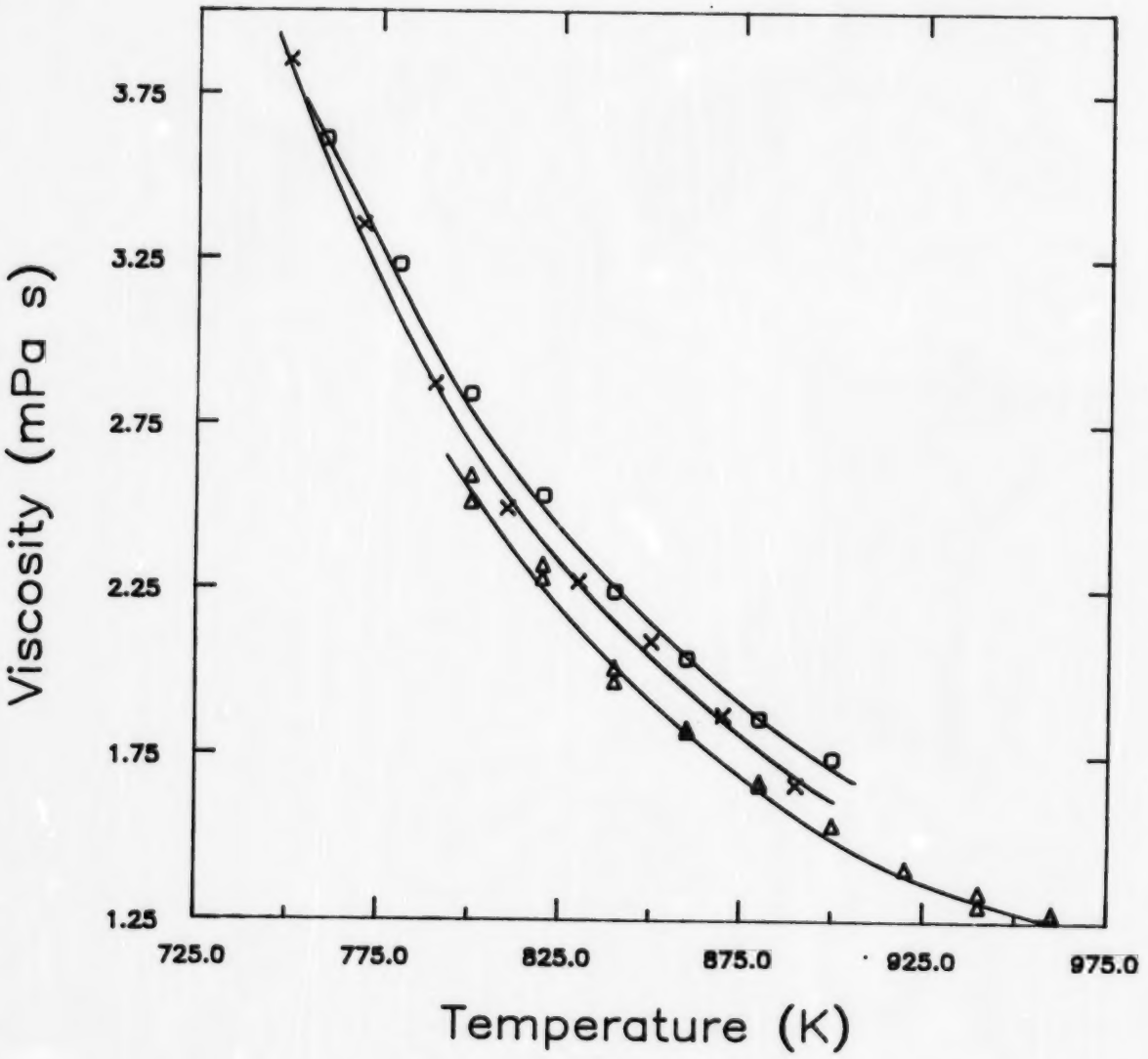

5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
(Reading/f(Density))^K
1.00
1.50
2.00
2.50
3.00
3.50
4.00
4.50
5.00
Viscosity (mPa s)

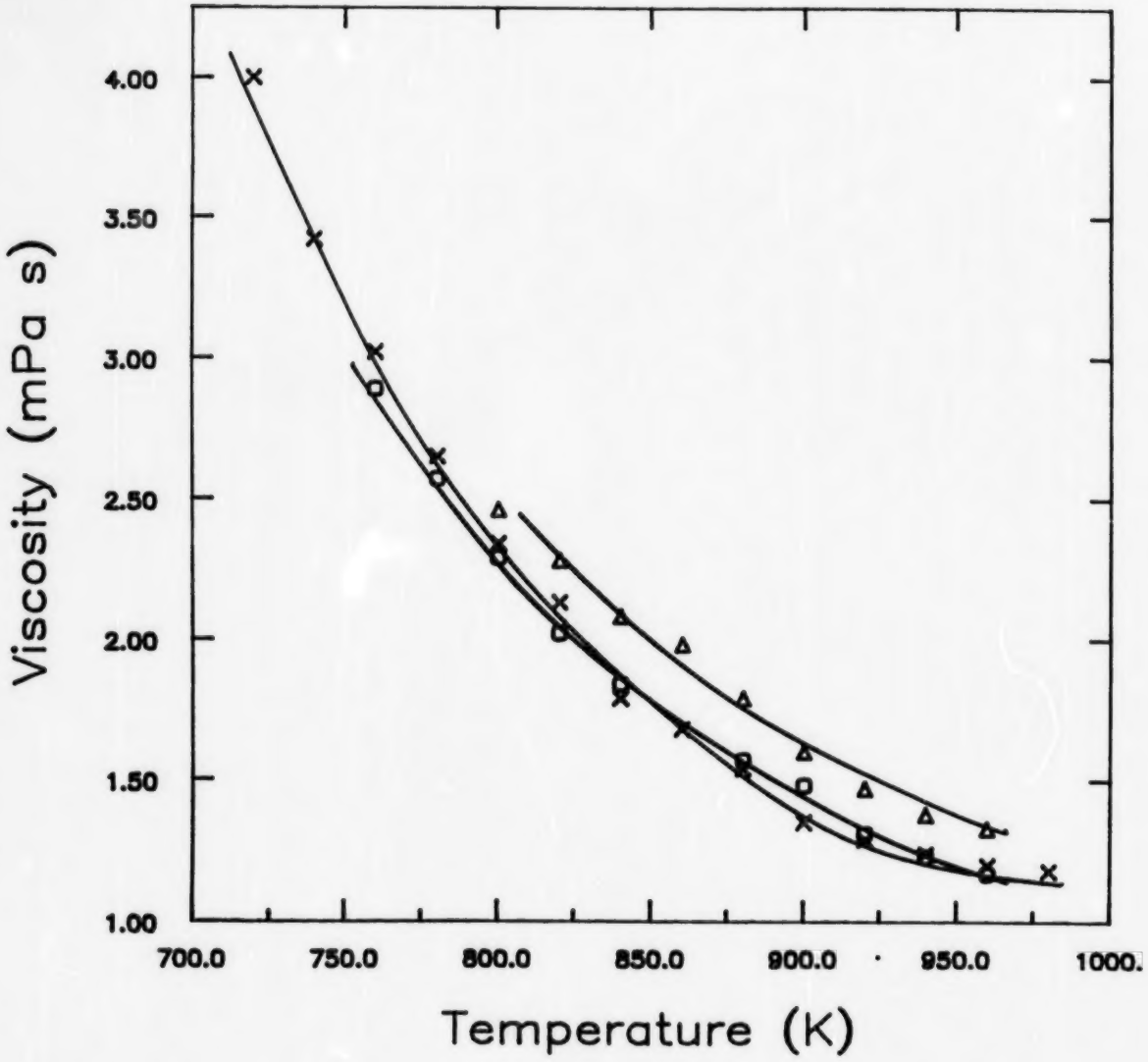

4.00
3.50
3.00
2.50
2.00
1.50
1.00
Viscosity (mPa s)
750.0
800.0
850.0
900.0
950.0
1000.
Temperature (K)

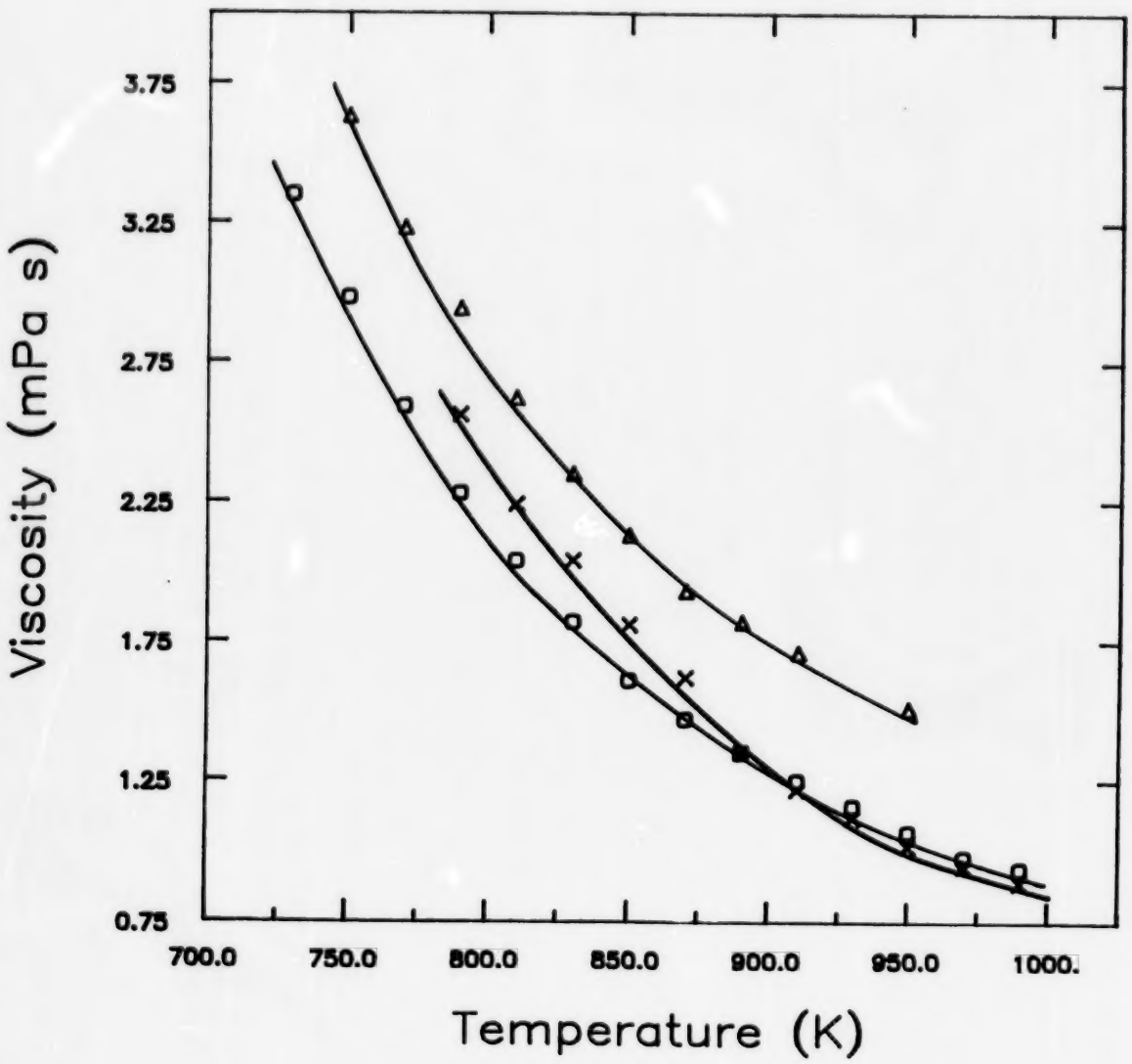

3.50
3.00
2.50
2.00
1.50
1.00
Viscosity (mPa s)
750.0
800.0
850.0
900.0
950.0
1000.
Temperature (K)

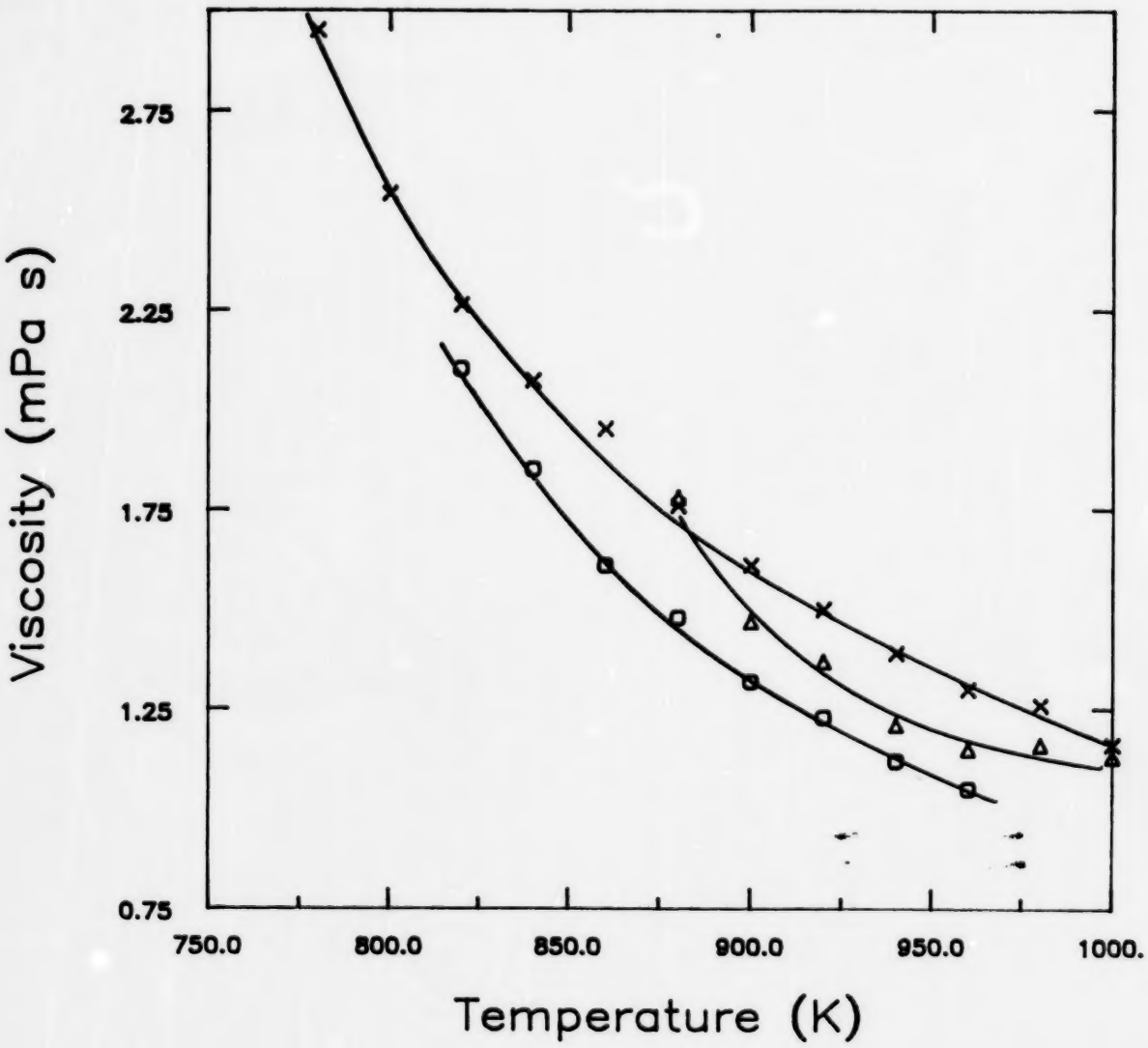

1.75
1.25
0.75
Viscosity (mPa s)
850.0
900.0
950.0
1000.
1050.
Temperature (K)


Viscosity (mPa s)
1.50
1.30
1.10
0.90
0.70
975.0
1025.
1075.
1125.
Temperature (K)


Viscosity (mPa s)
3.75
3.25
2.75
2.25
1.75
1.25
725.0
775.0
825.0
875.0
925.0
975.0
Temperature (K)


Viscosity (mPa s)
4.00
3.50
3.00
2.50
2.00
1.50
1.00
700.0
750.0
800.0
850.0
900.0
950.0
1000.
Temperature (K)


Viscosity (mPa s)
3.75
3.25
2.75
2.25
1.75
1.25
0.75
700.0
750.0
800.0
850.0
900.0
950.0
1000.
Temperature (K)


Viscosity (mPa s)
2.75
2.25
1.75
1.25
0.75
750.0
800.0
850.0
900.0
950.0
1000.
Temperature (K)